Bi $6s^2$ lone-pair-induced magnetic order in the quadruple perovskite $BiMn_7O_{12}$

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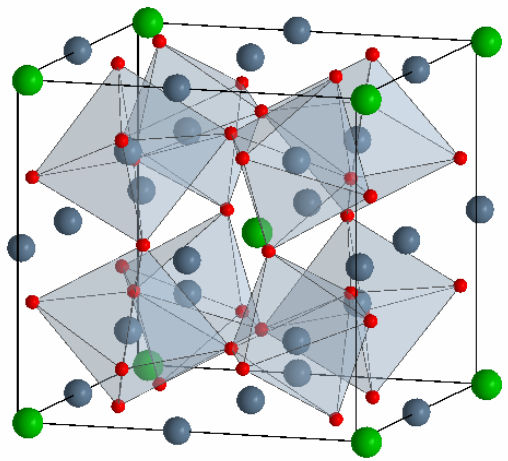

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OUTLINE

- Introduction and motivation:
  - Space group symmetry as control parameter of complex orderings in perovskite-like Jahn-Teller systems
  - Quadruple perovskites as model systems for mastering CMR and multiferroicity in manganese oxides
- Single-valent *quadruple perovskites* $LaMn_7O_{12}$ and $BiMn_7O_{12}$: comparison with *ordinary perovskites* $LaMnO_3$ and $BiMnO_3$
- $LaMn_7O_{12}$ and $BiMn_7O_{12}$:
  - High-pressure synthesis
  - Nuclear and magnetic structures
  - Transport and dielectric properties
- Role of Bi $6s^2$ lone pair on the magnetic structure and on the multiferroic properties of $BiMn_7O_{12}$
- Conclusions and perspectives

MOTIVATION

- Unique properties of perovskite-like manganese oxides:
  - Complex charge, spin and orbital orderings
  - Colossal magnetoresistance (CMR)
  - Multiferroicity
- Controversial structure-property relationships including:
  - JT distortions and mechanism of charge transport ($LaMnO_3$)
  - Effect of polar ions (e.g. Bi^{3+}) on the crystal structure and ferroelectricity (e.g. $BiMnO_3$)
  - …
- Challenges:
  - Complex pattern of (local) structural distortions
  - Controlling defects (e.g. oxygen stoichiometry)
  - …

▼ Can we find model systems with simple distortion patterns?

STRUCTURAL DISTORTIONS & GROUND STATE STABILITY IN PEROVSKITE-LIKE JAHN-TELLER (JT) MANGANESE OXIDES

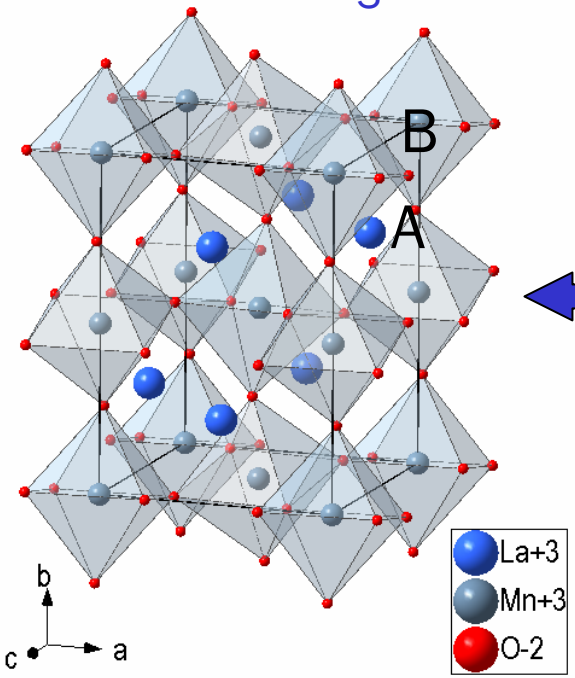
- *Main distortions of the ABO_3 perovskite structure:*
  - **Buckling** of the MnO_6 octahedra
  - **JT distortion** of the MnO_6 octahedra
- *Relevant geometrical parameters:*
  - Mn-O-Mn bond angle (buckling)
  - Mn-O bond distance (JT-driven)
- *Parametrization of electronic structure:*
  - t: transfer integral
  - U: Coulomb repulsion term (d^n-$d^n \rightarrow d^{n-1}$-d^{n+1})
  - Δ: Charge transfer energy (ligand-metal)

⇓

▼ Strength and sign of magnetic exchange interaction and charge transport mechanism (polaronic, vibronic,...)

COMPLEX DISTORTION PATTERNS IN ORDINARY PEROVSKITES

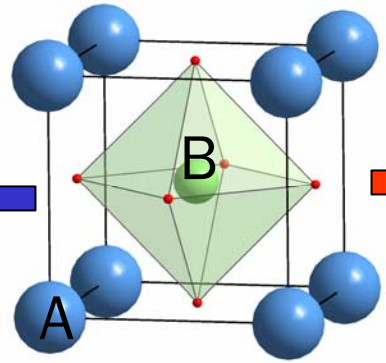
$LaMnO_3$



$GdFeO_3$-type (*Pbnm*):
$a \sim b \sim \sqrt{2}a_P$; $c \sim 2a_P$

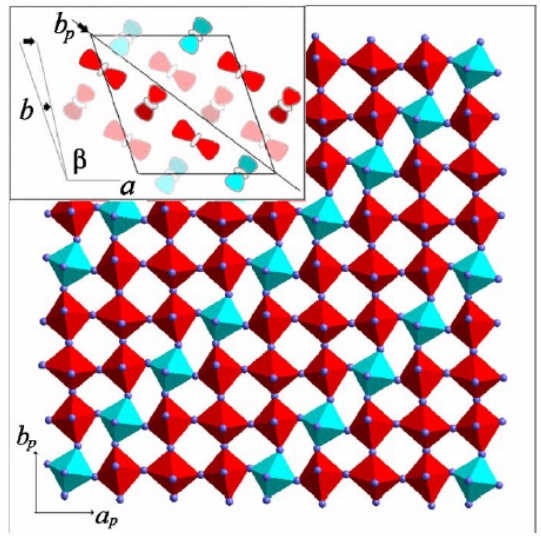
- Buckling **and** JT distortion of the BO_6 octahedra present
- Sizable *local* JT distortion even for $T > T_{JT}$=750 K (Sanchez *et al.*, 2003)
- Structure sensitive to O defects

ABO_3



Pristine ABO_3 (*Pm-3m*)

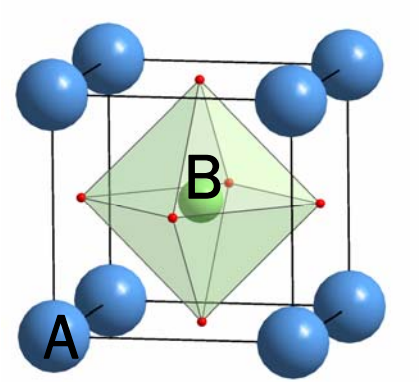
$BiMnO_3$



Space group: C2/c (?)
$a \sim b \sim c \sim 4a_P$

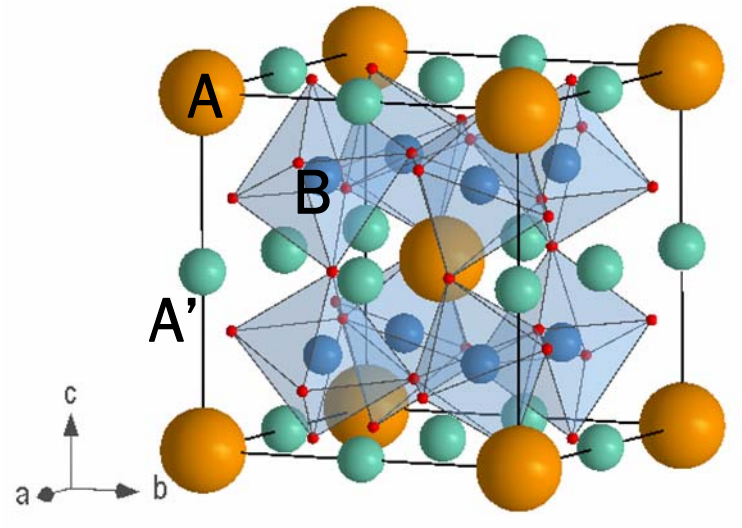
- Structure still controversial
- Comparatively large unit cell
- Link between -1 symmetry and possible multiferroicity?
- Sensitive to defects & strain

QUADRUPLE PEROVSKITES: ELEGANT DISTORTIONS



Pristine ABO_3 (*Pm-3m*)

Quadruple perovskite



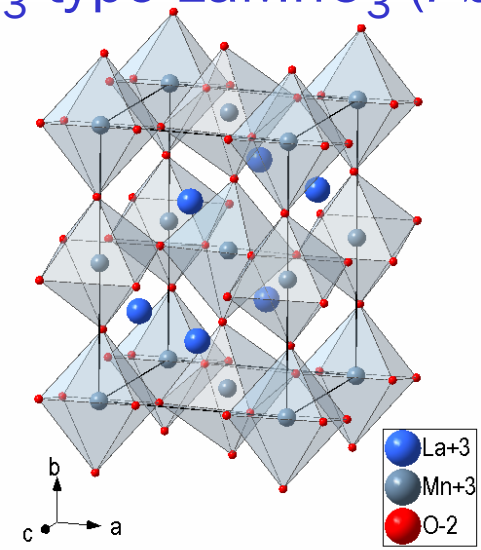
$CaCu_3Ti_4O_{12}$-type (*Im-3*):
$a \sim 2a_P$

(Marezio *et al.* 1973)
(Deschanvres *et al.* 1967)

- Crystallographic distinct A and A' sites
- A' site is JT active (JT distortion of A' site → doubling of a_P)
- Buckling and JT distortion of BO_6 octahedra occur <u>separately</u>:
  - **Rigid** buckling of **regular** BO_6 octahedra (cubic *Im-3* at high *T*)
  - JT distortion of the BO_6 octahedra at T_{JT}, *Im-3* → *I2/m*)

SITE SYMMETRY AND STRUCTURAL DISTORTIONS

Ordinary perovskite
$GdFeO_3$-type $LaMnO_3$ (*Pbnm*)

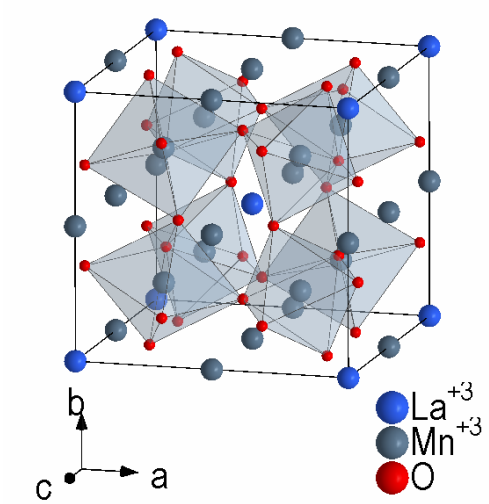


T=798 K > T_{JT}=750 K (O* phase)

Atom	*Pos*	*Site symm*	*x*	*y*	*z*
Mn1	4a	-1	0	0	0
O1	4c	.m.	**0.0687**	1/4	**0.4890**
O2	8d	1	**0.7257**	**0.0378**	**0.3038**

(Rodriguez-Carvajal *et al*., 1998)

Quadruple perovskite
$LaMn_7O_{12}$ (*Im-3*)



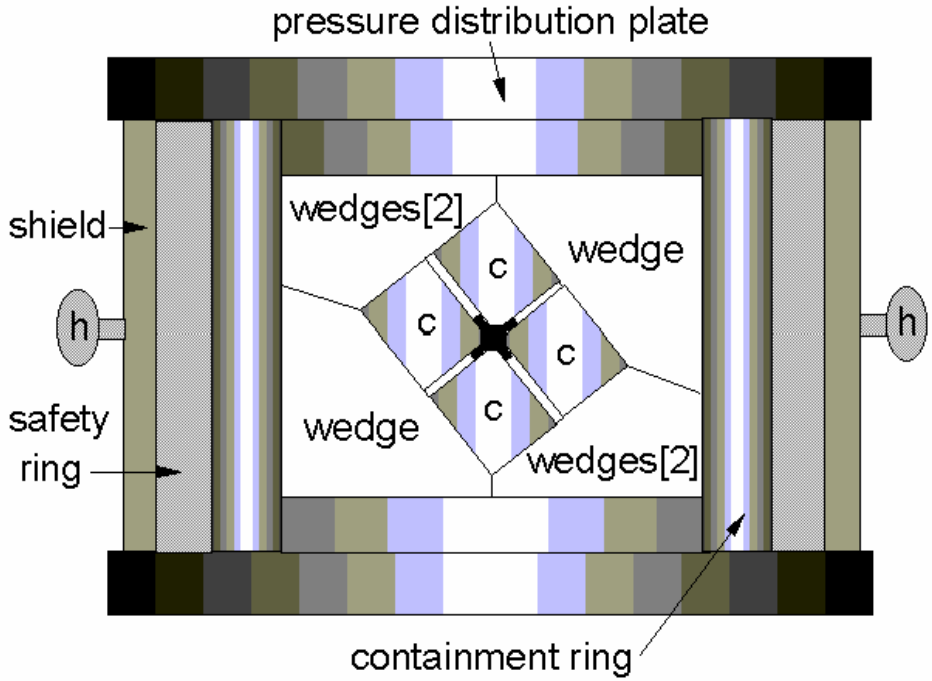
$T > T_{JT}$ = 650 K

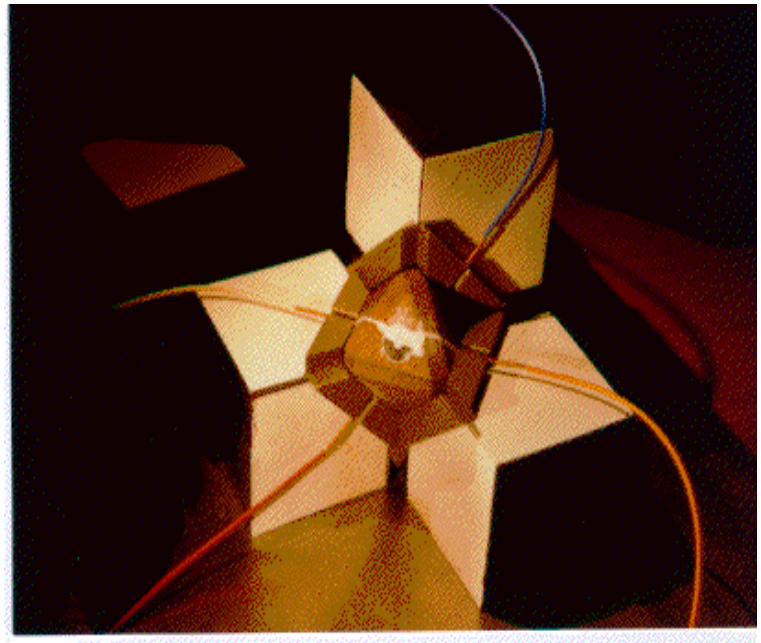
Atom	*Pos*	*Site symm*	*x*	*y*	*z*
Mn1(A')	6b	4/mm. m	1/2	0	0
Mn2(B)	8c	.-3m.	1/4	1/4	1/4
O1	24g	mm2 . .	**0.3131**	**0.1824**	0

(Prodi *et al*., 2009; Okamoto *et al*. 2009)

▼ Much more degrees of freedom for distortions in $GdFeO_3$-type!

MULTI-ANVIL HIGH-PRESSURE SYNTHESIS OF AMn_7O_{12} (*A*=La,Bi)

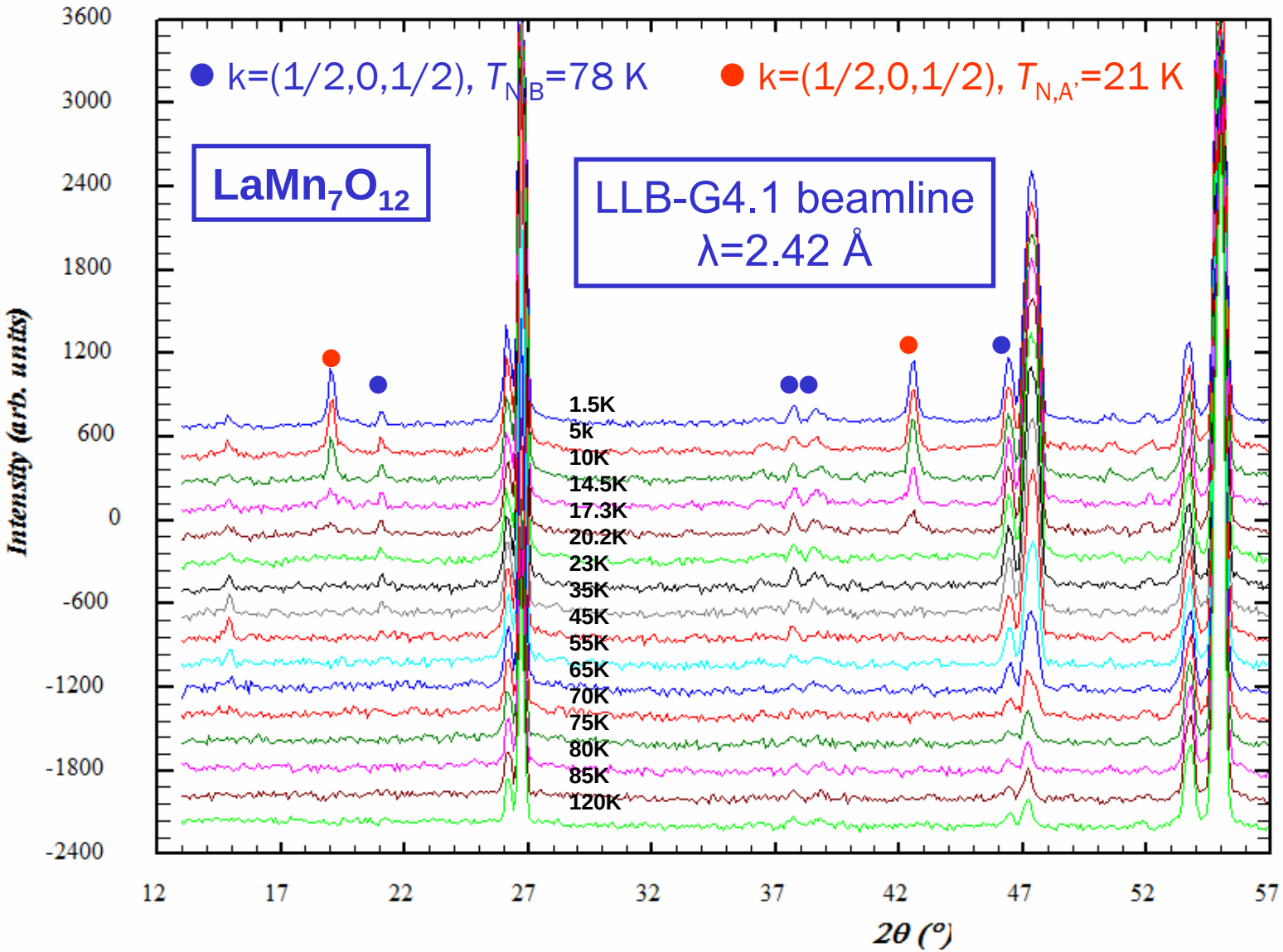




Walker *et al*. (1991)

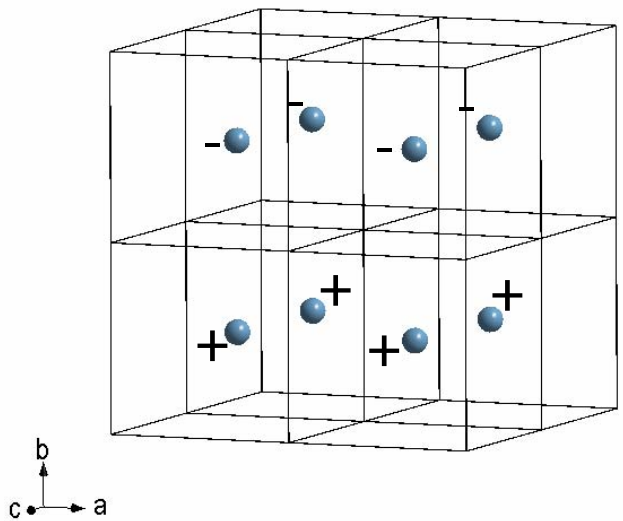
- Very high quasi-hydrostatic *P* up to 25 GPa
- Phase stability range for $LaMn_7O_{12}$ and $BiMn_7O_{12}$:
  - *P* = 4 GPa
  - *T* = 1000 °C
- Sintered powder samples >95% pure or 0.1-0.5 mm single crystals

MAGNETIC TRANSITIONS IN $LaMn_7O_{12}$



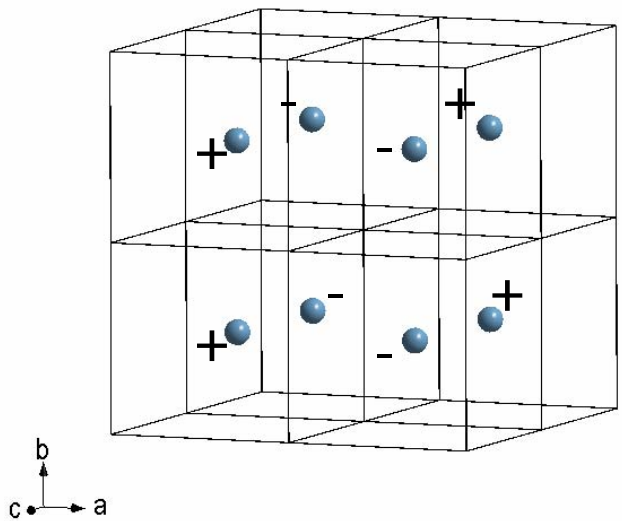
MAGNETIC STRUCTURE OF THE *B* SUBLATTICE: $LaMnO_3$ vs. $LaMn_7O_{12}$

A-type



$LaMnO_3$

C-type

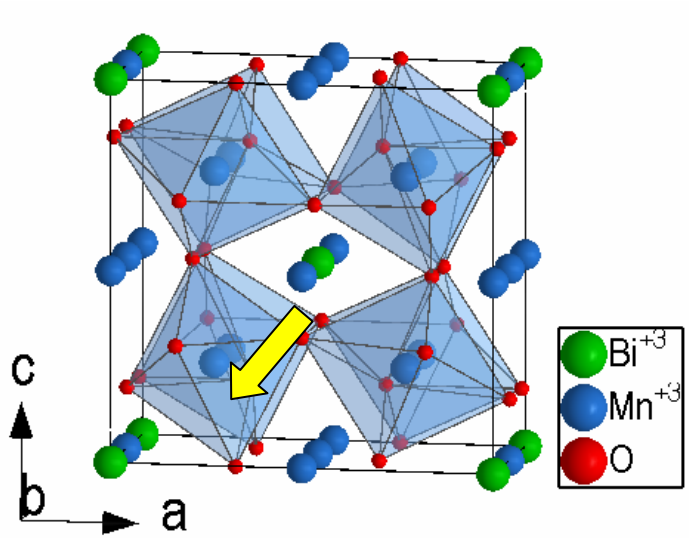


$LaMn_7O_{12}$

Prodi *et al*. (2009)

▼ Difference in magnetic structure reflects the different symmetry and the different JT distortion of the *B*-sites

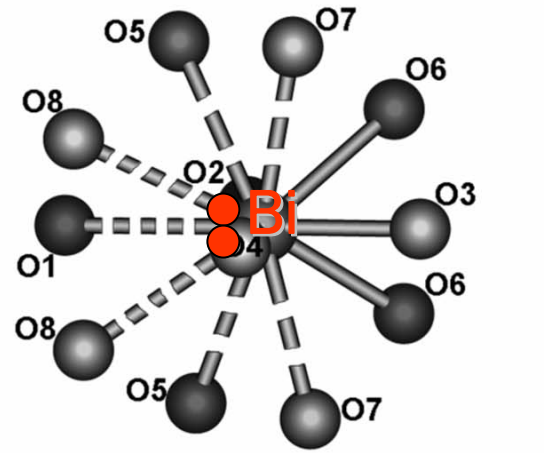
CENTROSYMMETRY *I2/m* → *Im* BREAKING IN $BiMn_7O_{12}$



$LaMn_7O_{12}$ $T<T_{JT}$=650 K (*I2/m*)

Atom	*Pos*	*Site symm*	*x*	*y*	*z*
La(A)	2a	2/m	0	0	0
Mn1(A')	2c	2/m	1/2	0	0
Mn2(B)	4e	-1	1/4	1/4	1/4

(Prodi *et al.*, 2009)



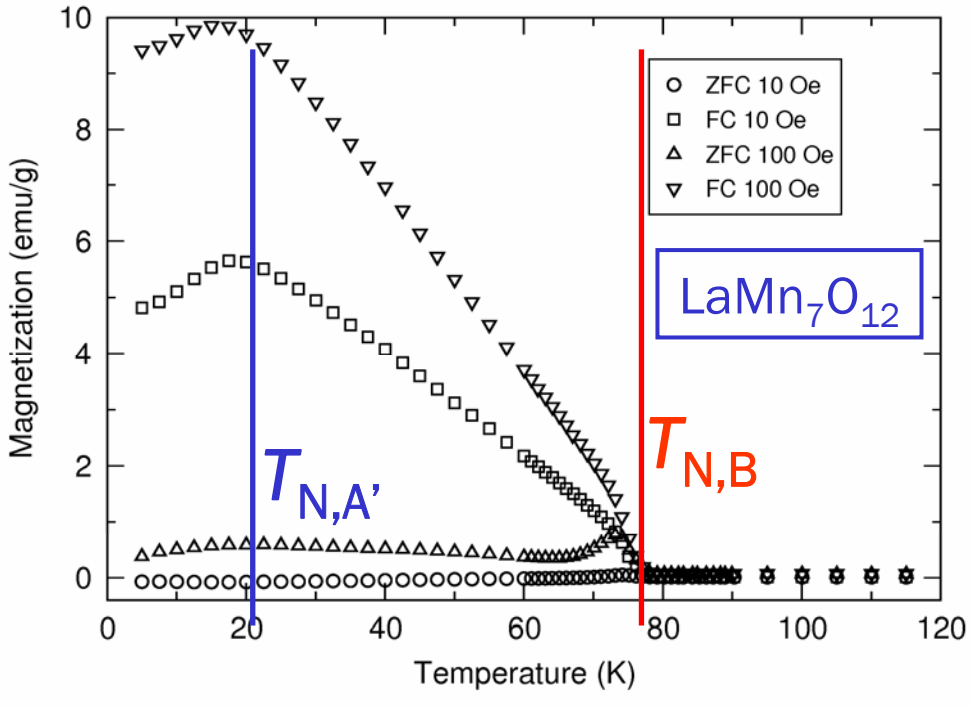
(Mezzadri *et al.*, 2009)

$BiMn_7O_{12}$ $T<T_{JT}$=? (*Im*)

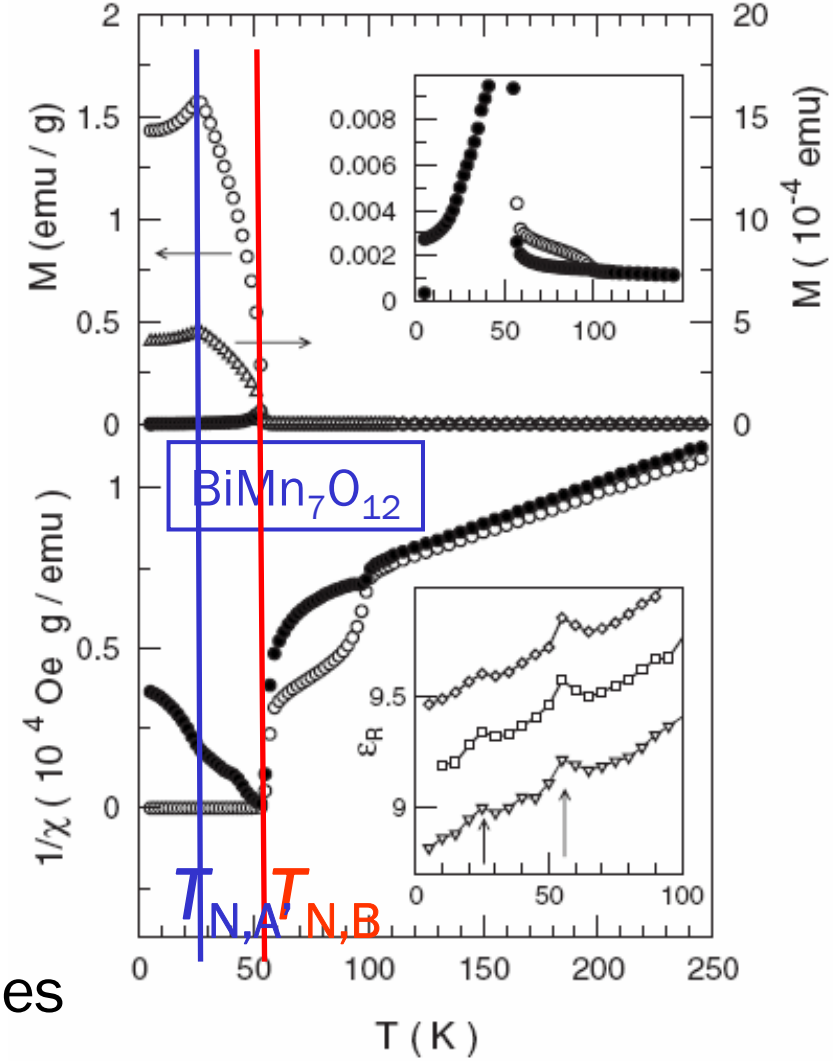
Atom	*Pos*	*Site symm*	*x*	*y*	*z*
Bi(A)	2a	m	0	0	0
Mn1(A')	2a	m	0.4713	0	0.4846
Mn2(B)	4b	1	0.2258	0.7419	0.2367

(Mezzadri *et al.*, 2009)

$LaMn_7O_{12}$ vs. $BiMn_7O_{12}$: SIMILAR MAGNETIC PROPERTIES BUT…



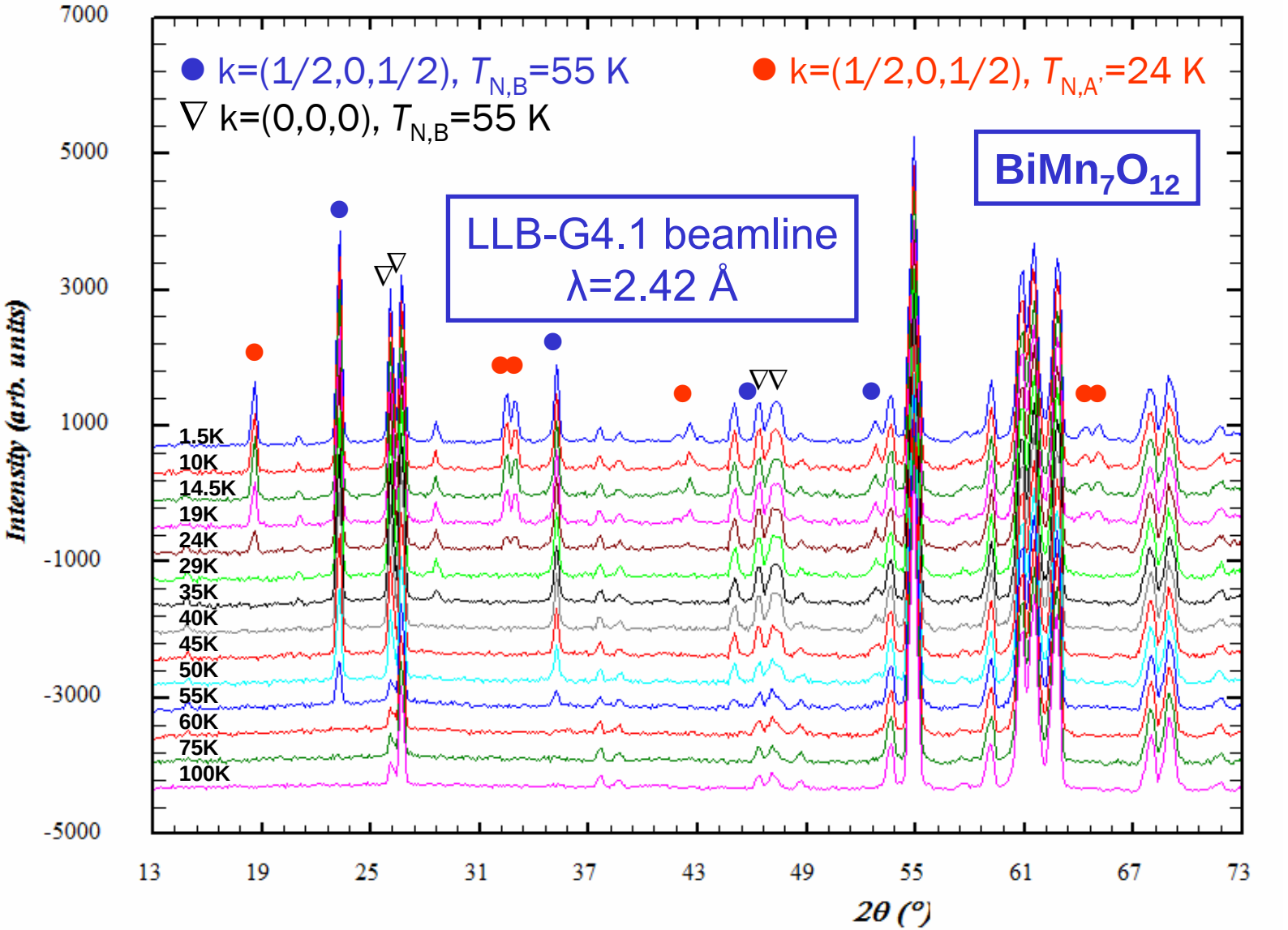
(Prodi *et al.*, 2009)



(Mezzadri *et al.*, 2009)

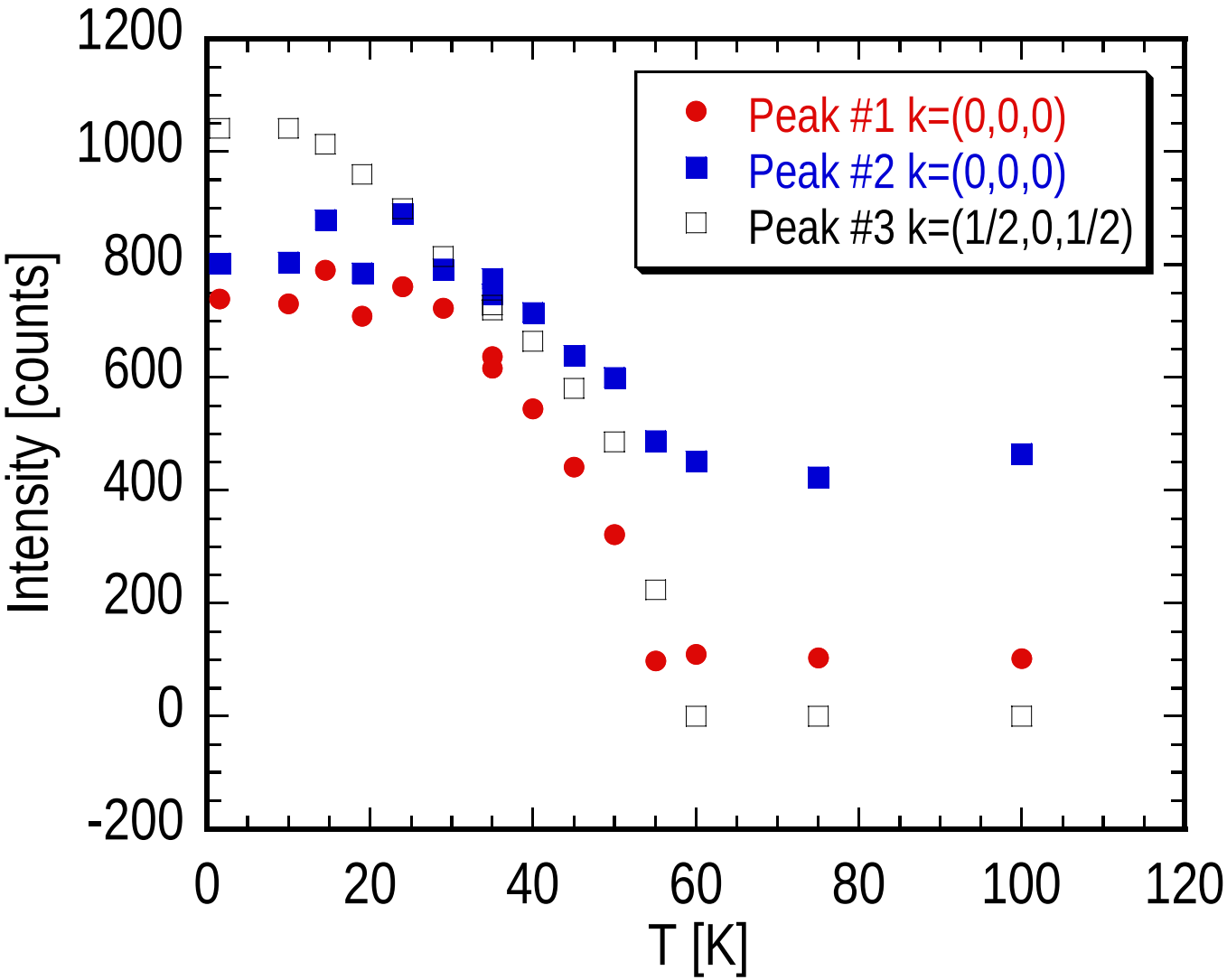
- Independent AFM ordering of A' and B Mn^{3+} sites in both cases
- FM-like response at $T_{N,B}$ in both cases
- Anomaly of ε at $T_{N,B}$ in $BiMn_7O_{12}$

UNUSUAL MAGNETIC STRUCTURE OF $BiMn_7O_{12}$



(Rousse *et al.*, 2009)

MAGNETIC ORDERING OF THE *B*-Mn^{3+} IONS IN $BiMn_7O_{12}$: COEXISTENCE OF TWO AFM AND FM PROPAGATION VECTORS



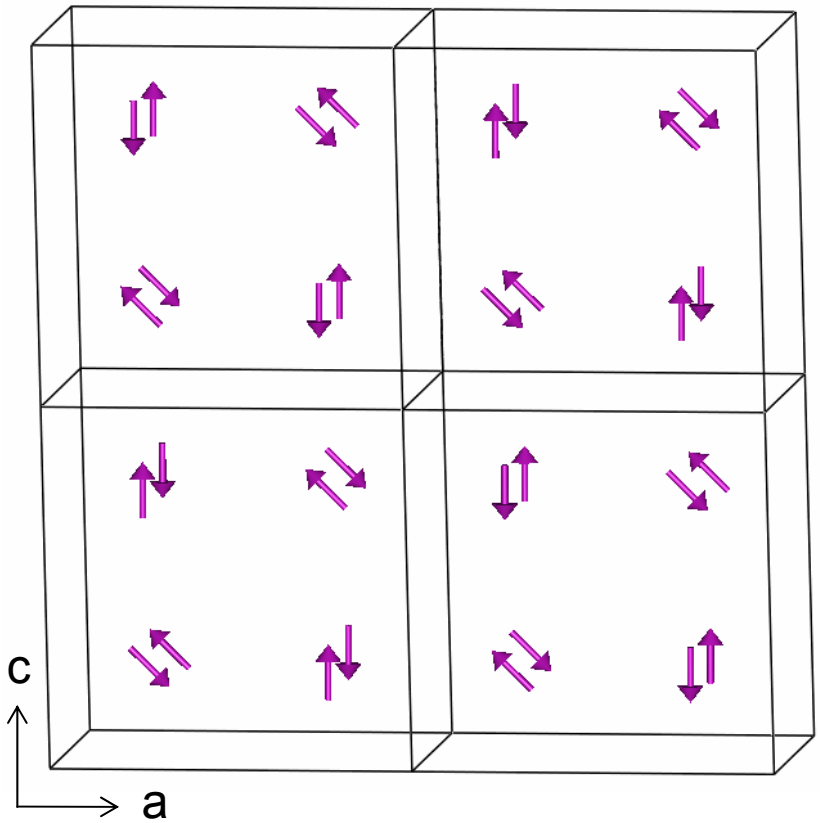
(Rousse *et al.*, 2009)

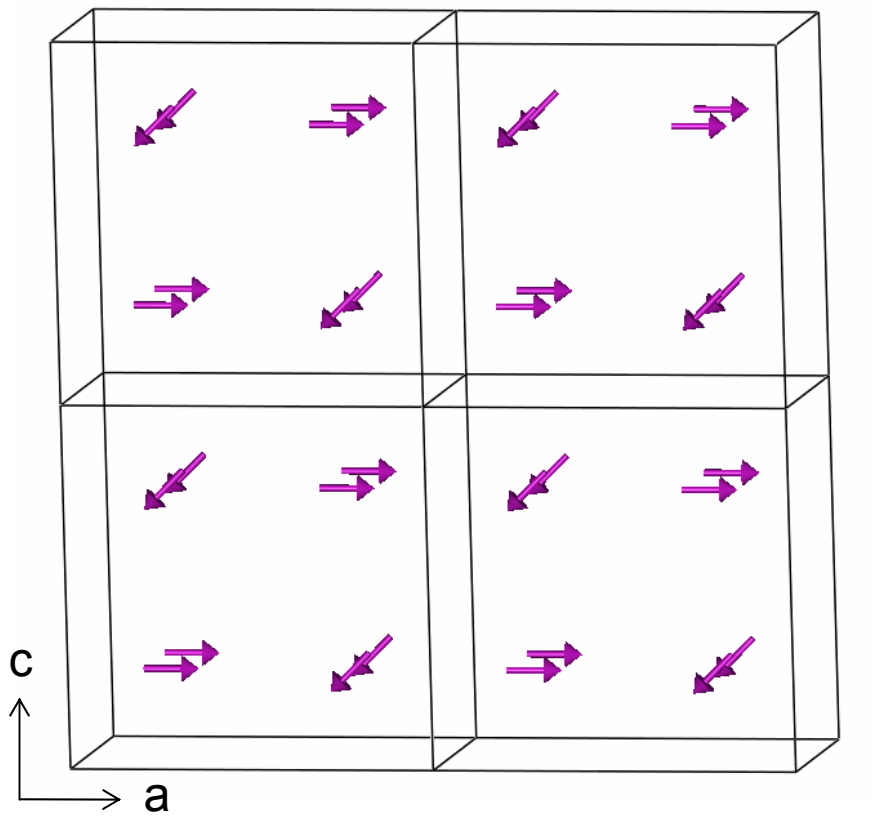
$BiMn_7O_{12}$: MAGNETIC STRUCTURE OF THE Mn^{3+} B-SUBLATTICE

Refinement requires two distinct propagation vectors:

k=*(1/2,0,1/2) (AFM ordering) and* **k**=*(0,0,0) (FM ordering)*

Proposed structure at 35 K





▼ Superposition of AFM k=(1/2,0.1/2) & FM k=(0,0,0) structure: coupling between AFM and ferroelectric order parameters?

CONCLUSIONS

- Quadruple perovskites: a new playground for studying competing orderings in perovskite-like manganese oxides:
  - buckling and JT distortions of MnO_6 octahedra separated
  - proper JT distortion at T_{JT} (cubic-monoclinic)
- Single-valent $LaMn_7O_{12}$ and $BiMn_7O_{12}$: high-pressure phases stable at 4 GPa, 1000 °C
- >95% pure powders or single crystals up to ~0.5 mm
- Independent AFM orderings of *A*' and *B* sites
- $LaMnO_3$ vs. $LaMn_7O_{12}$: topologically different magnetic structure of *B* Mn^{3+} ions: role of symmetry and JT distortion of the *B*-sites
- $LaMn_7O_{12}$ vs. $BiMn_7O_{12}$: topologically different magnetic structure of *B* Mn^{3+} ions
- $BiMn_7O_{12}$: Breaking of -1 $\rightarrow$ coupling between AFM and ferrolectric order parameters? (Role of Bi $6s^2$ lone pair!)

$LaMn_7O_{12}$ & $BiMn_7O_{12}$: PERSPECTIVES & FUTURE WORK

- Larger single crystals: full determination of magnetic structure
- Inelastic scattering: dynamics of JT phonons and spin excitations
- Magnetic structure: use local probes
- Study multiferroic properties of $BiMn_7O_{12}$